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The Distribution of 2-Thenoyltrifluoroacetone between Several Organic Solvents and an Aqueous Solution and Its Extraction of Sodium(I) into Methyl Isobutyl Ketone

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Aqueous solutions containing sodium hydroxide and sodium perchlorate at various mixing ratios, 1 M Na(OH, ClO_4), were equilibrated with several organic solvents containing 2-thenoyltrifluoroacetone (TTA) at 25°C. From the measurements of the hydrogen-ion concentration of the aqueous phase, the $(K_D+1)K_a^{-1}$ values, where K_D is the distribution constant and K_a is the acid dissociation constant of TTA, were obtained; they were, $10^{7.17}$ (hexane), $10^{7.74}$ (CCl_4), $10^{8.01}$ (C_6H_6) and $10^{8.17}$ ($CHCl_3$). From the values of K_D obtained in another study, the value of K_a was determined to be $10^{-6.28}$. However, a much lower value than that expected was obtained for the MIBK system; this was due to the extraction of sodium(I) with TTA. The extraction was also confirmed by the distribution experiments of sodium(I). The extraction constant, $K_{ex}=[NaA]_{org}/[Na^+][A^-]$ (where A^- is the TTA anion), was found from these results to be $10^{0.86}$ in 1 M $NaClO_4$ and $10^{0.79}$ at an infinite dilution.

The solvent extraction of alkali metal ions with chelating extractants is usually poor except for that of lithium(I).[1-4] However, it was pointed out by Healy[3] that the extraction of alkali metal ions with 2-thenoyltrifluoroacetone (TTA)[3] and dibenzoylmethane[4] is very much enhanced by adduct formation (synergism); thus, even sodium(I) can be extracted to some extent with these chelating reagents if a neutral adduct-forming ligand, such as trioctylphosphine oxide, triphenylphosphine oxide, tributylphosphate, N,N-dibutylacetamide, ethylhexyl alcohol or nitromethane, is added.

The present authors have made a series of studies of the acid dissociation and two-phase distribution of several β-diketones. When the organic phase was nonpolar solvent, the chemical behavior of these reagents agreed with that statistically expected. However, when the solvent was methyl isobutyl ketone (MIBK), a deviation from the statistical expectation was found.

After an analysis, it was concluded that the above deviation is due to an extraction of the sodium(I) with TTA. This was also confirmed from the distribution ratio of sodium(I), measured by using a radioactive tracer.

Experimental

The sodium-24 tracer was obtained from the Japan Atomic Energy Research Institute as a sodium chloride solution. The TTA and MIBK were obtained from the Dojindo & Co. and the Tokyo Kasei Co., Ltd., respectively. The MIBK was washed several times with 0.1 M perchloric acid and with water, and then washed several times with 0.1 M sodium hydroxide and again with water. The sodium perchlorate was prepared from sodium carbonate and perchloric acid and was recrystallized three times from water. The other reagents were of an analytical grade. The sodium hydroxide solution was prepared by the dilution of its 50% aqueous solution with decarbonated water. A weighed portion of TTA was dissolved in an organic solvent, stored at least one day before the experiment, and then used as the stock solution.

All of the procedures were carried out in a thermostatted room at 25±0.3°C. Twenty-ml glass-stoppered tubes were used to equilibrate the two phases. A 5-ml portion of the TTA solution of an organic solvent, and a 5-ml portion of an aqueous solution which contained the 1 M sodium ion, and perchlorate and hydroxide ions at a certain molar ratio, 1 M Na(OH, ClO_4), were placed in the tubes. In the MIBK system, the two phases in the tube were placed on a rotating framework (20 rpm), agitated for three hr, and then centrifuged. In the other systems, the two phases were vigorously shaken for several minutes and then centrifuged. The hydrogen-ion concentration (in stoichiometric units) of the aqueous phase were determined potentiometrically with a glass electrode.

The experiment with the radioactive tracer was carried out as follows. The initial aqueous phase contained various amounts of sodium hydroxide and the sodium tracer. A 5-ml portion of this aqueous phase and a 5-ml portion of the MIBK solution, which contained an amount of TTA equivalent to the sodium hydroxide in the aqueous phase were placed in the tubes. The two phases were vigorously shaken for 3 min and then centrifuged. A 2-ml portion was pipetted from each phase and transferred into a small test tube. The γ-radioactivity of the sample was determined with a well-type scintillation counter (NaI). The distribution ratio was calculated as follows;

$$D=\frac{\gamma\text{-count-rate per ml of the org. phase}}{\gamma\text{-count-rate per ml of the aq. phase}}$$

Statistical

The acid dissociation constant and the two phase-distribution constants of a weak acid, HA, can be written as;

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = [H^+][A^-][HA]^{-1} \qquad (1)$$

$$HA \rightleftharpoons HA_{(org)}$$

$$K_D = [HA]_{org}[HA]^{-1} \qquad (2)$$

The ratio of these two values can be determined by a two-phase titration method[5] or by measurements of

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[1] G. A. Guter, G. S. Hammond, *J. Amer. Chem. Soc.*, **78**, 5166 (1956).

[2] R. F. Apple, J. C. White, *Talanta*, **13**, 43 (1966).

[3] T. V. Healy, *J. Inorg. Nucl. Chem.*, **30**, 1025 (1968).

[4] T. V. Healy, *ibid.*, **31**, 499 (1969).

[5] D. Dyrssen, *Svensk, Kem. Tidskr.*, **64**, 213 (1952),

the hydrogen-ion concentration of the aqueous phase, which initially contained various amounts of hydroxide ions and which were equilibrated with an organic phase containing an excess of the acid to the hydroxide ion.[6]

The statistical treatment for the latter method is as follows. In the following equations, the initial concentration of the acid in the organic phase will be denoted by $C_{\mathrm{HA(org)}}$, and that of sodium hydroxide in the aqueous phase, by C_{OH}. The volumes of the two phases are always the same, and we assume no complex formation in the aqueous phase.

When no extraction of sodium salt occurs, the following equations can be obtained from Eqs. (1) and (2):

$$\begin{aligned} C_{\mathrm{HA(org)}} &= [\mathrm{A^-}] + [\mathrm{HA}] + [\mathrm{HA}]_{\mathrm{org}} \\ &= [\mathrm{A^-}]\,(1 + (K_{\mathrm{D}}+1)K_{\mathrm{a}}^{-1}[\mathrm{H^+}]) \end{aligned} \tag{3}$$

If $-\log [\mathrm{H^+}]$ is not very high (*e.g.*, if $-\log [\mathrm{H^+}]$ is below 11), it can be regarded that $C_{\mathrm{OH}}=[\mathrm{A^-}]+[\mathrm{OH^-}]\simeq[\mathrm{A^-}]$. Then, C_{OH} can be introduced into Eq. (3) instead of $[\mathrm{A^-}]$ and we obtain:

$$C_{\mathrm{HA(org)}}C_{\mathrm{OH}}^{-1} - 1 = (K_{\mathrm{D}}+1)K_{\mathrm{a}}^{-1}[\mathrm{H^+}] \tag{4}$$

On the other hand, when the sodium salts are extracted, the extraction equilibrium can be written as;

$$\mathrm{Na^+} + \mathrm{A^-} \rightleftarrows \mathrm{NaA_{(org)}}$$

$$K_{\mathrm{ex}} = [\mathrm{NaA}]_{\mathrm{org}}[\mathrm{Na^+}]^{-1}[\mathrm{A^-}]^{-1} \tag{5}$$

The initial concentration can then be written as (the other species in the organic phase, such as the dimer, are neglected):

$$\begin{aligned} C_{\mathrm{HA(org)}} &= [\mathrm{A^-}] + [\mathrm{HA}] + [\mathrm{HA}]_{\mathrm{org}} \\ &\quad + [\mathrm{NaA}]_{\mathrm{org}} + [\mathrm{A^-}]_{\mathrm{org}} \end{aligned} \tag{6}$$

When no dissociation in the organic phase is assumed, Eq. (6) can be rewritten as:

$$\begin{aligned} C_{\mathrm{HA(org)}} &= [\mathrm{A^-}] + [\mathrm{NaA}]_{\mathrm{org}} \\ &\quad + (K_{\mathrm{D}}+1)K_{\mathrm{a}}^{-1}[\mathrm{A^-}][\mathrm{H^+}] \end{aligned} \tag{7}$$

Furthermore, when the concentration of the sodium ion can always be regarded as unity and when $-\log [\mathrm{H^+}]$ is not very high (*e.g.*, when $[\mathrm{OH^-}]<10^{-3}$, in other words, $[\mathrm{Na^+}]_{\mathrm{initial}} - [\mathrm{NaA}]_{\mathrm{org}} \simeq 1\ \mathrm{M}$):

$$C_{\mathrm{OH}} = [\mathrm{A^-}] + [\mathrm{NaA}]_{\mathrm{org}} = [\mathrm{A^-}](1+K_{\mathrm{ex}}) \tag{8}$$

From Eqs. (7) and (8), the following equation is obtained:

$$C_{\mathrm{HA(org)}}C_{\mathrm{OH}}^{-1} - 1 = (K_{\mathrm{D}}+1)K_{\mathrm{a}}^{-1}(K_{\mathrm{ex}}+1)^{-1}[\mathrm{H^+}] \tag{9}$$

Since the $C_{\mathrm{HA(org)}}$ and C_{OH} values are known, and since the $[\mathrm{H^+}]$ value can be determined by potentiometry, the $(K_{\mathrm{D}}+1)K_a^{-1}(K_{\mathrm{ex}}+1)^{-1}$ value can be determined from a set of experimental data, and when the values of K_{D} and K_a can be obtained by separate experiments, the K_{ex} value can be determined.

The distribution data of the second experiments, which were carried out by using a radioactive tracer, were treated as follows. Since the initial amount of sodium hydroxide is equivalent to that of the weak acid, TTA, in these systems, the $[\mathrm{Na(I)}]_{\mathrm{org,total}}=[\mathrm{TTA}]_{\mathrm{org,total}}$, and $[\mathrm{Na(I)}]_{\mathrm{total}}=[\mathrm{TTA}]_{\mathrm{total}}$ relations are always established. Provided that there is no dissociation of the species in the organic phase and no association of those in the aqueous phase, and furthermore, provided that the amount of the TTA in the HA form produced by the hydrolysis of $\mathrm{A^-}$ in the aqueous phase is much smaller than that of $\mathrm{A^-}$, the following equations can be obtained:

$$[\mathrm{Na(I)}]_{\mathrm{org,total}} = [\mathrm{NaA}]_{\mathrm{org}} \tag{10}$$

$$[\mathrm{Na(I)}]_{\mathrm{total}} = [\mathrm{Na^+}] = [\mathrm{A^-}] \tag{11}$$

$$D = [\mathrm{NaA}]_{\mathrm{org}}[\mathrm{Na^+}]^{-1} \tag{12}$$

From the above equations and Eq. (5):

$$K_{\mathrm{ex}} = D[\mathrm{A^-}]^{-1} = D[\mathrm{Na^+}]^{-1} \tag{13}$$

When the distribution ratio is determined by radiometry, the value of $[\mathrm{Na^+}]$ can be obtained as:

$$[\mathrm{Na^+}] = C_{\mathrm{OH}}(D+1)^{-1} \tag{14}$$

and from this value of $[\mathrm{Na^+}]$, K_{ex} can be obtained by means of Eq. (13).

Results

Distribution Measurements. Table 1 gives the results of the distribution measurements. As may be seen from Eq. (13), the distribution ratio decreases with the decrease in $[\mathrm{Na^+}]$ (and, at the same time, with that in C_{OH}). Since the ionic strength in the aqueous phase is not controlled in these systems, the extraction constants determined cannot be directly compared with each other. However, from these results, the following conclusions can be reached: (i) Part of the sodium (I) in the aqueous phase is extracted into MIBK with TTA. (ii) The value of K_{ex} increases with the decrease in the aqueous sodium-ion concentration and reaches a definite value. Thus, the K_{ex} at an infinite dilution can be estimated to be $10^{0.79}$.

Another series of distribution measurements were also carried out in systems where the electrolyte concentration in the aqueous phase was kept at 1 M by using sodium perchlorate. However, since sodium perchlorate is also to some extent extractable into the organic

TABLE 1. DISTRIBUTION OF SODIUM(I) BETWEEN MIBK AND AQUEOUS PHASE CONTAINING SODIUM SALT OF TTA (NO PERCHLORATE) DETERMINED BY RADIOMETRY[a)]

$C_{\mathrm{OH}}(=C_{\mathrm{HA(org)}})$	$\log D$	$\log [\mathrm{Na^+}]$	$\log K_{\mathrm{ex}}$[b)]
2.0×10^{-1}	-0.45	-0.83	0.38
1.0×10^{-1}	-0.62	-1.09	0.47
5.0×10^{-2}	-0.77	-1.37	0.60
3.0×10^{-2}	-0.93	-1.57	0.64
2.0×10^{-2}	-1.07	-1.74	0.67
1.0×10^{-2}	-1.33	-2.02	0.69
8.0×10^{-3}	-1.36	-2.12	0.76
6.0×10^{-3}	-1.48	-2.24	0.76
4.0×10^{-3}	-1.62	-2.41	0.79
2.0×10^{-3}	-1.92	-2.70	0.78

a) The total amount of sodium ion is equivalent to TTA and the ionic strength in the aqueous phase is not controlled.
b) $\log D - \log [\mathrm{Na^+}]$. Since the ionic strength in the aqueous phase changes, direct comparison of these data to each other is not suitable, especially in the higher $[\mathrm{Na^+}]$ region.

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[6] T. Sekine and D. Dyrssen, *Anal. Chim. Acta*, **37**, 217 (1967).

TABLE 2. HYDROGEN ION CONCENTRATION IN THE AQUEOUS PHASE AS A FUNCTION OF INITIAL SODIUM HYDROXIDE CONCENTRATION

C_{OH}	Hexane		Carbon tetrachloride		Benzene		Chloroform		MIBK	
	a	b	a	b	a	b	a	b	a	b
6.98×10^{-2}	7.52	7.15	8.07	7.71	8.34	7.98	8.50	8.14	7.88	7.52
5.98×10^{-2}	7.33	7.16	7.89	7.72	8.17	7.99	8.32	8.15	7.77	7.60
4.98×10^{-2}	7.18	7.18	7.73	7.74	8.01	8.01	8.17	8.17	7.67	7.67
3.99×10^{-2}	6.99	7.17	7.58	7.76	7.84	8.02	8.02	8.19	7.56	7.74
2.99×10^{-2}	6.80	7.17	7.41	7.78	7.68	8.05	7.83	8.20	7.33	7.70
average		7.17		7.74		8.01		8.17		(7.65)

Volumes of the two phases are the same, the aqueous phase is 1 M $NaClO_4$.

The acid dissociation constant for TTA in 1 M $NaClO_4$ at 25°C is obtained to be $10^{-6.28}$ from the above constants and the values of K_D for each solvent.[8]

$a=-\log[H^+]$, $b=\log(K_D+1)/K_a$.

TABLE 3. HYDROGEN ION CONCENTRATION IN THE AQUEOUS PHASE IN MIBK-1 M $NaClO_4$ SYSTEM AS A FUNCTION OF INITIAL SODIUM HYDROXIDE CONCENTRATION, AND THE EQUILIBRIUM CONSTANTS CALCULATED[a)]

C_{OH}	$C_{HA(org)}=0.05$ M		$C_{HA(org)}=0.1$ M		$C_{HA(org)}=0.2$ M	
	$-\log[H^+]$	$\log\frac{(K_D+1)}{K_a(K_{ex}+1)}$	$-\log[H^+]$	$\log\frac{(K_D+1)}{K_a(K_{ex}+1)}$	$-\log[H^+]$	$\log\frac{(K_D+1)}{K_a(K_{ex}+1)}$
4.99×10^{-2}	—	—	7.67	7.68	7.09	7.57
4.39×10^{-2}	8.14	7.28<	—	—	—	—
3.99×10^{-2}	8.00	7.40<	7.56	7.74	—	—
2.99×10^{-2}	7.79	7.62	7.33	7.70	6.88	7.63
2.39×10^{-2}	7.61	7.65	—	—	—	—
1.99×10^{-2}	7.47	7.65	7.09	7.69	—	—
1.40×10^{-2}	7.35	7.76	6.89	7.68	6.55	7.67
9.97×10^{-3}	7.09	7.69	6.75	7.71	—	—
8.97×10^{-3}	7.03	7.69	—	—	—	—
7.98×10^{-3}	—	—	6.68	7.74	6.25	7.63
6.98×10^{-3}	6.89	7.68	6.58	7.70	—	—
5.98×10^{-3}	—	—	6.58	7.78	6.15	7.66
4.99×10^{-3}	6.72	7.68	6.42	7.70	—	—
3.99×10^{-3}	6.60	7.66	6.32	7.70	5.95	7.64
2.99×10^{-3}	6.46	7.66	6.18	7.69	—	—
1.99×10^{-3}	6.34	7.72	5.97	7.66	5.65	7.65
average		7.68		7.71		7.64

$K_{ex}=[NaA]_{org}[Na^+]^{-1}[A^-]^{-1}$ $K_{ex_0}=[NaA]_{org}[H^+][Na^+]^{-1}[HA]_{org}^{-1}$

a) The equilibrium constant $\log(K_D+1)K_a^{-1}(K_{ex}+1)^{-1}$ is concluded to be 7.68.

From this value and the value of $(K_D+1)K_a^{-1}$ for this MIBK system determined in another study[8], the following extraction constants were obtained; $K_{ex}=10^{0.86}$, $K_{ex_0}=10^{-7.73}$.

phase,[7] a correction for this effect was necessary. In this case, as the accuracy of the experiments was not satisfactorily enough to make such a correction, no difinite value of K_{ex} could be obtained from these experiments.

Potentiometric Measurements. The value, $(K_D+1)K_a^{-1}$, obtained by introducing the values of $C_{HA(org)}$, C_{OH}, and $[H^+]$ into Eq. (4) agreed with the value computed by using the K_D and K_a^{-1} values experimentally obtained when the solvent was hexane, carbon tetrachloride, benzene, or chloroform. Thus we concluded that there was no extraction of sodium (I) with TTA into these solvents. Table 2 shows the values of $-\log[H^+]$ at equilibrium against the initial concentration of sodium hydroxide in the aqueous phase, C_{OH}, when the initial concentration of TTA in the organic phase, $C_{HA(org)}$, is 1.00×10^{-1} M. Table 2 also shows the $(K_D+1)K_a^{-1}$ values calculated by means of Eq. (4). Although a slight increase in $(K_D+1)\times K_a^{-1}$ with the decrease in C_{OH} is observed, it may be concluded that the values are nearly constant in each system.

The distribution constants of TTA in these systems were determined in another study in the authors' laboratory by the spectrophotometric method.[8] The values obtained were $10^{0.85}$, hexane; $10^{1.43}$, carbon tetrachloride; $10^{1.73}$, benzene; and $10^{1.89}$, chloroform With these distribution constants and the $(K_D+1)\times K_a^{-1}$ value obtained for each solvent in Table 2, the values of K_a were calculated to be $10^{-6.27}$, $10^{-6.30}$,

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[7] T, Sekine and T. Ishii, This Bulletin, **44**, 275 (1971).

[8] Y. Hasegawa, *et al.*, unpublished work,

$10^{-6.28}$, and $10^{-6.27}$, from the results in the hexane, carbon tetrachloride, benzene, and chloroform systems, respectively. The acid dissociation constant of TTA in the 1 M sodium perchlorate solution at 25°C was thus estimated to be $10^{-6.28}$ as the average of these values.

The distribution constant of TTA between MIBK and 1 M sodium perchlorate had also been determined separately[8] to be $10^{2.31}$, and from the values of this K_D and the above K_a value, the log $(K_D+1)K_a^{-1}$ value in this system was expected to be $10^{8.59}$. However, as may be seen from Table 2, the value experimentally obtained, $10^{7.65}$ is about one-tenth of the expected value. The deviation may well be explained by the extraction of sodium with TTA which had already been demonstrated by the tracer experiments. Table 3 gives the values of $-\log[H^+]$ at equilibrium against the initial concentration of sodium hydroxide in the aqueous phase when the initial TTA concentrations in MIBK, $C_{HA(org)}$, are 0.05, 0.1, and 0.2 M and the values of the equilibrium constant, $(K_D+1)K_a^{-1}\times(K_{ex}+1)^{-1}$. The value of K_{ex} in Eq. (5) was calculated from this constant, and from the above $(K_D+1)\times K_a^{-1}$ value for the MIBK system, to be $10^{0.86}$.

The constant for metal extraction with chelating extractants is usually given by the following equation:

$$Na^+ + HA_{(org)} \rightleftharpoons NaA_{(org)} + H^+$$

$$K_{ex_0} = [NaA]_{org}[H^+][Na^+]^{-1}[HA]^{-1}_{org} \qquad (15)$$

From Eqs. (5) and (15), the following relation can be obtained;

$$K_{ex_0} = K_{ex}K_aK_D^{-1} \qquad (16)$$

Thus, K_{ex_0} in Eq. (15) can be calculated, from the constants cited above, to be $10^{-7.73}$.

Discussion

In order to make an analysis of the chemical equilibria in metal extraction system with a chelating extractant, the $(K_D+1)K_a^{-1}$ (when $K_D \gg 1$, $K_DK_a^{-1}$ can be used) is very important.[9] This value can be obtained naturally if the values of K_a and K_D can be found in the literature. However, these values are different when the ionic concentration in the aqueous phase is different, and the latter constant, K_D of course, is different in different solvents.

Although the two-phase titration method[5] seems to be applicable to such determinations of $(K_D+1)K_a^{-1}$, the simplified method demonstrated in this study also seems to be very useful for such a purpose, as has already been pointed out.[6] The usefulness of this method may be concluded from the fact that the values of K_a of TTA in 1 M sodium perchlorate calculated from the results of the four series of independent experiments using the different solvents shown in Table 2 are identical with each other.

It is well known that MIBK is a very good solvent for the TTA extraction of several metal ions, because the extraction is much enhanced by the use of this solvent over that using various non-polar solvents. For example, the extraction of alkaline earth ions with TTA is very effective when the solvent is MIBK, as was first reported by Kiba and Mizukami.[10] This enhancement has been quantitatively explained, in terms of adduct TTA chelate formation.[6]

The fact found in this study, that sodium(I) is extracted with TTA only when the solvent is MIBK, seems to indicate that the extraction of sodium with TTA due to an adduct formation of the chelate complex with MIBK, as in the case of the extraction of sodium(I) with TTA in benzene containing various neutral adduct-forming ligands.[3] Healy pointed out that two molecules of the adduct-forming ligand combine with one TTA sodium(I) chelate. In the present study, this solvation number could not be determined.

The value of the extraction constant, K_{ex_0}, in Eq. (5), $10^{-7.73}$, is not large, although it is much larger than that when the solvent is pure benzene, $10^{-11.16}$.[3] Thus, as has been described, the determination of K_{ex} from the distribution data when the aqueous phase is 1 M sodium perchlorate was not successful. On the other hand, it is very remarkable that the deviation of the hydrogen-ion-concentration data of the extraction experiments is quite large (one pH unit); thus, a reasonable extraction constant could be determined from the data.

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[9] T. Sekine and N. Ihara, This Bulletin, **44**, 2942 (1971).

[10] T. Kiba and S. Mizukami, *ibid.*, **31**, 1007 (1958).